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Japanese Unexamined Patent Application Laid Open H3-74415

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(43) Published 29th March, 1991**Number of Claims: One****Request for Examination: Not yet requested****Number of Pages in the Japanese Text: Nine****(54) Title of the Invention: Method for the production of highly stereoregular polypropylene****(21) Application Number: H1-209540****(22) Date of Application: 15th August, 1989****(72) Inventor: Takashi NOZAKI**

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SPECIFICATION

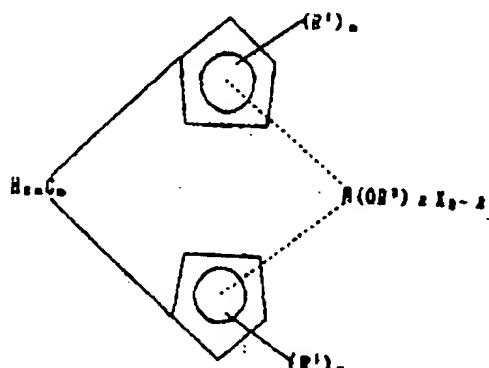
1. Title of the Invention

Method for the production of highly stereoregular polypropylene

2. Scope of the Patent Claim

A method for the production of highly stereoregular polypropylene characterized in that use is made of a catalyst comprising (A) an organometallic compound which can be represented by the general formula (1) indicated below and (B) an inorganic oxide support on which an alumoxane has been loaded

General Formula:



(In this formula, R¹ are hydrocarbyl groups which have from 1 to 20 carbon atoms and two R¹ groups may, when present at adjacent positions on the cyclopentadienyl ring, form a carbon ring, and R² is a hydrocarbyl group or a thioaryl group, and when there are two such groups they may be joined together either directly with a carbon atom within each group or via a sulphur atom, M is titanium, zirconium or hafnium, X is a hydrocarbyl group or a halogen atom, n is an integer of value from 1 to 4, m is 0 or an integer of value from 1 to 4, and ℓ is 0 or an integer of value 1 or 2.)

3. Detailed Description of the Invention

Industrial Field of Application

The invention concerns a method whereby polypropylene which has high stereoregularity and excellent granular properties is produced in high yield using a catalyst in which a catalyst component comprising a specified transition metal compound and a catalyst component where an alumoxane has been loaded on an inorganic oxide support are combined.

Prior Art

In the past it was known that catalysts comprising methyl alumoxane and zirconocene, for example ethylenebis(indenyl)zirconium dichloride, which is sterically fixed have a high activity and provide poly- α -olefins which have high degree of stereoregularity. (Japanese Unexamined Patent Publication Laid Open 61-130314) Furthermore, it was known that the particle properties of the highly stereoregular poly- α -olefins which are produced was improved by using a catalyst comprising a combination of methyl alumoxane and a catalyst component where the zirconocene has been loaded on an inorganic oxide such as silica. (Japanese Unexamined Patent Publication Laid Open 63-66206)

Problems to be Resolved by the Invention

Ways of permitting the production of highly stereoregular polypropylene with sufficiently high activity and thus enabling the catalyst removal process to be omitted with a catalyst system comprising alumoxane and metallocene which has been sterically fixed have come under close scrutiny, but there are various problems when such processes are converted into industrial technologies and production on a scale which is thought to provide a very uniform catalyst system ensuring that the form of the particles of polymer powder is not disrupted has been indicated as one serious problem. Furthermore, many attempts have been made to resolve this problem using methods where the metallocene side is loaded on an inorganic oxide, but in this case there is a problem in that the activity is greatly reduced.

Means of Resolving These Problems

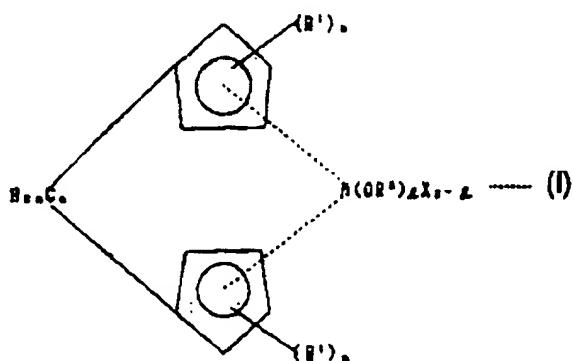
As a result of thorough research carried out with a view to resolving the abovementioned problem, the inventors had found that highly stereoregular polypropylene which had excellent particle characteristics could be obtained with comparatively little loss of activity when a method in which an organic aluminium component was loaded on an inorganic oxide already discovered by the inventors (Japanese Unexamined Patent Publication Laid Open 61-276805) was used in the aforementioned catalyst system. As a result of further investigation of the method of loading the organic aluminium component on an inorganic oxide support it has been discovered that by carrying out polymerization after removing the unreacted organic aluminium component the particle characteristics are improved even more, and that by loading methylalumoxane after bringing an organic aluminium compound into contact with the inorganic oxide support beforehand, a polymer which has extremely

good particle characteristics is obtained without reducing the activity, and the invention is based upon these discoveries.

That is to say, the invention is:

(1) A method for the production of highly stereoregular polypropylene characterized in that, a catalyst comprising (A) an organometallic compound which can be represented by the general formula (1) indicated below, and (B) an inorganic oxide support on which alumoxane has been loaded is used as a catalyst for the polymerization of propylene in the presence of a catalyst and the production of highly stereoregular polypropylene.

General Formula (I):



(In this formula, R¹ are hydrocarbyl groups which have from 1 to 20 carbon atoms and two R¹ groups may, when present at adjacent positions on the cyclopentadienyl ring, form a carbon ring, and R² is a hydrocarbyl group or a thioaryl group, and when there are two such groups they may be joined together either directly with a carbon atom within each group or via a sulphur atom, M is titanium, zirconium or hafnium, X is a hydrocarbyl group or a halogen atom, n is an integer of value from 1 to 4, m is 0 or an integer of value from 1 to 4, and ℓ is 0 or an integer of value 1 or 2.)

(2) A method for the production of highly stereoregular polypropylene, according to (1) above, in which the aforementioned (B) is a component which has been obtained by loading alumoxane, and especially methyl alumoxane, after bringing an organic aluminium compound into contact beforehand with the inorganic oxide support.

The invention is described in detail below.

The catalysts which are used in the method of this invention are formed from a combination of the aforementioned (A) and (B) components, and organometallic

compounds which can be represented by the aforementioned general formula (I) are used for the said (A) component.

Each of the cyclopentadienyl groups in the aforementioned general formula (I) may be substituted with from 1 to 4 R¹ groups, which is to say hydrocarbyl groups which have from 1 to 20 carbon atoms. Actual examples of the hydrocarbyl groups include aliphatic, alicyclic and aromatic hydrocarbyl groups such as the methyl, ethyl, propyl, butyl, isobutyl, t-butyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, cetyl, phenyl and cyclohexyl groups. Furthermore, two R¹ groups which are present at adjacent position on a cyclopentadienyl ring may form a carbon ring, thereby forming, together with the cyclopentadienyl ring, an indenyl group or a hydrogenated indenyl group. In this invention, the use of compounds which have such an indenyl group or hydrogenated indenyl group for the (A) component is especially desirable. Moreover, the number of carbon atoms in the alkylene group which is bonded to the two cyclopentadienyl group is from 1 to 4, and examples of such groups include both linear chain and branched alkylene groups such as the methylene, ethylene, 1,3-propylene, 1,2-propylene, 1,4-butylene and 2,3-butylene groups, but from among these the ethylene group is especially desirable.

Furthermore, M in the said general formula (I) is titanium, zirconium or hafnium, and from among these zirconium and hafnium are preferred, and zirconium is especially desirable.

R² in the aforementioned general formula (I) is a hydrocarbyl group or a thioaryl group, and when it is a hydrocarbyl group it may be, for example, a methyl group, an ethyl group, a propyl group, a butyl group, an isobutyl group, a t-butyl group, an amyl group, an isoamyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, a cetyl group, a phenyl group or a substituted phenyl group. Furthermore, where there are two R² groups they may be bonded together directly between carbon atoms in each group or via a sulphur atom.

X in the aforementioned general formula (I) is a hydrocarbyl group or a halogen atom, and actual examples include aliphatic and aromatic hydrocarbyl groups such as the methyl, ethyl, propyl, butyl, isobutyl, t-butyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, cetyl, and phenyl groups for example, and halogen atoms such as chlorine, bromine and iodine for example, but from among these chlorine is especially desirable.

Actual examples of compounds which can be represented by the aforementioned general formula (I) include methylenebis(cyclopentadienyl)titanium dichloride, ethylenebis(cyclopentadienyl)titanium dichloride, propylenebis(cyclopentadienyl)titanium dichloride, tetramethylethylenebis(cyclopentadienyl)titanium dichloride, ethylenebis(indenyl)titanium dichloride, ethylenebis(tetrahydroindenyl)titanium dichloride, methylenebis(cyclopentadienyl)zirconium dichloride, ethylenebis(cyclopentadienyl)zirconium dichloride, propylenebis(cyclopentadienyl)zirconium dichloride, tetramethylethylenebis(cyclopentadienyl)zirconium dichloride, ethylenebis(indenyl)zirconium dichloride, ethylenebis(indenyl)zirconium dimethyl, ethylenebis(indenyl)zirconium diethyl, ethylenebis(indenyl)zirconium dimethoxide, ethylenebis(indenyl)zirconium diethoxide, ethylenebis(indenyl)zirconium dipropoxide, ethylenebis(indenyl)propoxyzirconium chloride, ethylenebis(indenyl)zirconium dibutoxide, ethylenebis(indenyl)propoxyzirconium chloride, ethylenebis(tetrahydroindenyl)dichloride (sic), ethylenebis(tetrahydroindenyl)zirconium dipropoxide, ethylenebis(tetrahydroindenyl)zirconium dibutoxide, ethylenebis(tetrahydroindenyl)propoxyzirconium chloride, ethylenebis(indenyl)zirconium-1,1'-bi-2-phenolate, ethylenebis(indenyl)zirconium-1,1'-bi-2-naphtholate, ethylenebis(indenyl)zirconium-4,4'-dimethyl-6,6'-di-t-butyl-2,2'-methylenediphenolate, ethylenebis(indenyl)zirconium-4,4'-dimethyl-6,6'-di-t-butyl-2,2'-thiophenolate, ethylenebis(tetrahydroindenyl)zirconium-1,1'-bi-2-phenolate, ethylenebis(tetrahydroindenyl)zirconium-1,1'-bi-2-naphtholate, ethylenebis(tetrahydroindenyl)zirconium-4,4'-dimethyl-6,6'-di-t-butyl-2,2'-methylenediphenolate, ethylenebis(tetrahydroindenyl)zirconium-4,4'-dimethyl-6,6'-di-t-butyl-2,2'-thiophenolate, ethylenebis(indenyl)hafnium dichloride and ethylenebis(tetrahydroindenyl)hafnium dichloride, and from among these ethylenebis(indenyl)zirconium dichloride and ethylenebis(indenyl)hafnium dichloride are preferred.

These metallocene compounds can be produced using known methods, such as the methods disclosed or cited in Japanese Unexamined Patent Applications Laid Open 61-130314 and 63-251405 for example.

The (B) component is described below.

For the (B) component, an alumoxane is loaded on an inorganic oxide support. A porous inorganic oxide is preferred for the support, and actual examples

include silica, silica-alumina, alumina, magnesia and such like materials, but the use of silica is preferred. A support of which the specific surface area is at least $200 \text{ m}^2/\text{g}$ is especially desirable. No particular limitation is imposed upon the surface hydroxyl group content of these inorganic oxides, but it is preferably within the range from 0.05 to 5 mmol OH/g, and this range can be obtained easily, for example, by drying the abovementioned inorganic oxides at a temperature of from 150 to 700°C in a vacuum, or under a current of air or nitrogen.

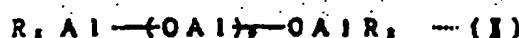
The carrying out of a treatment in which an organic aluminium compound is first brought into contact with the support before the reaction in which the alumoxane is loaded on the inorganic oxide is especially desirable in this invention.

Actual examples of the organic aluminium compound include trialkyl aluminium compounds such as trimethylaluminium, triethylaluminium and triisobutylaluminium, alkenylaluminium compounds such as isopropenylaluminium, alkoxidized alkylaluminium compounds such as dimethylaluminium methoxide and diethylaluminium ethoxide, halogenated alkylaluminium compounds such as diethylaluminium chloride and ethylaluminium sesquichloride, and alumoxane compounds such as methylalumoxane and isobutylalumoxane, and the trialkylaluminium compounds are preferred.

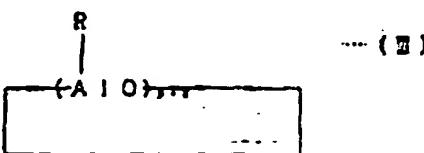
The proportion in which the organic aluminium compound is brought into contact with the inorganic oxide support in this invention, calculated as aluminium atom, is from 1 to 20 mmol Al, and preferably from 1 to 10 mmol Al, per 1 g of inorganic oxide support.

The organic aluminium compounds which can be represented by general formula (II) or general formula (III) below, for example, can be cited as actual examples of the alumoxanes which are loaded on the inorganic oxide support.

General Formulae (II) and (III)



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(R in this formula is a hydrocarbyl group which has from 1 to 4 carbon atoms, and p is an integer of value from 1 to 40.)

Examples of R in the abovementioned general formulae (II) and (III) include lower alkyl groups such as the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and t-butyl groups, for example, and from among these the methyl group is especially desirable, and a value of at least 5 is desirable for p. Most desirably p has a value of from 5 to 20.

Such alumoxanes can be obtained generally by reacting trialkylaluminium compounds with water, but the method for their preparation is not subject to any particular limitation and any of the known methods can be used.

For example there is a method in which trialkylaluminium is dissolved in a hydrocarbon solvent and brought into gradual contact with an equivalent amount of water, and a method in which hydrated copper sulphate or hydrated aluminium sulphate is suspended in a hydrocarbon solvent and hydrolysis is carried out by admixing the trialkylaluminium, using from one to three times the amount of water of crystallization.

The proportion in which alumoxane is brought into contact with the inorganic oxide support in this invention is, calculated as aluminium, from 1 to 40 mmol Al, and preferably from 1 to 20 mmol Al, per 1 g of inorganic oxide support.

Any of the methods (1) to (4) indicated below can be used to prepare an inorganic oxide support on which alumoxane has been loaded, but of these method (2) is preferred.

- (1) The method in which the alumoxane and the inorganic oxide support are reacted in an inert hydrocarbon solvent such as toluene.
- (2) The method in which an organic aluminium compound and the inorganic oxide support are mixed, or mixed and heated, under nitrogen in an inert hydrocarbon solvent such as toluene and then a reaction is carried out with an alumoxane.
- (3) The method in which an organic aluminium compound and alumoxane are mixed, or mixed and heated, under nitrogen in an inert hydrocarbon solvent such as toluene and then reacted with the inorganic oxide support.
- (4) The method in which the alumoxane and the inorganic oxide support are mixed, or mixed and heated, under nitrogen, in an inert hydrocarbon solvent such as toluene and then a reaction is carried out with an organic aluminium compound.

Isolation of the solid component obtained by means of the abovementioned reaction by filtration or decantation followed by thorough washing using an inert hydrocarbon solvent such as toluene to remove the unreacted material and by-products, for example, is especially desirable in this invention. The aluminium atom is generally loaded in an amount of from 2 to 10 mmol per 1 g of the catalyst component (B) obtained in this way.

In this invention, those from among these catalyst components (B) on which from 1 to 10 mmol of aluminium atom of alumoxane origin is loaded are preferred.

The amount of each catalyst component used is described below.

The aforementioned (A) component in the method of this invention is preferably used in a form where it has been rendered soluble in inert hydrocarbon solvents such as toluene, and it is used in a proportion such that the concentration as the transition metal ion is generally from 10^{-10} to 10^{-1} mol/l, and preferably from 10^{-7} to 10^{-2} mol/l. On the other hand, the aforementioned (B) component is used in a proportion with respect to the said (A) component such that the aluminium atom/transition metal atom ratio is generally within the range from 1 to 10^6 , and preferably within the range from 1 to 10^4 . Moreover, in this invention the activity is sufficiently high and polymerization can be carried out even in those cases where the aluminium atom/transition metal atom ratio is low, in the range from 1 to 200.

The way in which the catalyst comprising the aforementioned (A) component and (B) component is formed and the method used and not subject to any particular limitation in this invention. That is to say, in the method of this invention, for example, the catalyst components (A) and (B) may be supplied separately to the polymerization system, or the two catalyst components may be supplied to the polymerization system after being pre-mixed. However, in this invention the catalyst components (A) and (B) are preferably supplied separately to the polymerization system.

No particular limitation is imposed upon the method of polymerization used in the invention, and the polymerization can be carried out either in the liquid phase or in the gas phase. When the polymerization is carried out in the liquid phase an inert solvent such as benzene or toluene may be used for the reaction medium, but propylene itself can also be used as the reaction medium. Furthermore, no particular limitation is imposed upon the polymerization system, and the polymerization can be carried out using a batch-type system or using a continuous polymerization system.

The polymerization temperature in this invention is generally selected from within the range from -80°C to 100°C, and preferably from within the range from -20°C to 80°C.

The polypropylene obtained in this way has a high degree of stereoregularity, with a proportion of the meso-meso arrangement in the overall triad chain of at least 90%.

Illustrative Examples

Illustrative examples of the invention are described below, but the invention is not limited in any way by these illustrative examples.

Moreover, the mm proportion in the illustrative examples and in the tables is the proportion of meso-meso arrangement in all triad chains obtained by dissolving the polymer in o-dichlorobenzene and carrying out a ^{13}C -NMR analysis at 135°C using a GX-270Q manufactured by Nippon Denshi, and it is a measure of the stereoregularity of the polymer which has been produced.

Example 1

(1) Alumoxane Synthesis

The alumoxane synthesis was carried out in the following way under a current of nitrogen gas in accordance with Example 1 of Japanese Unexamined Patent Application Laid Open 58-19309.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (37.5 g, 0.15 mol, corresponding to 0.75 mol of H_2O) was suspended in 250 ml of toluene and then 50 ml (0.52 mol) of trimethylaluminium were added and the mixture was reacted from 24 hours at 20°C, with stirring. The production of methane gas was observed during the reaction. After the reaction, the copper sulphate was filtered off and, on removing the toluene from the filtrate, 13.0 g (44% of the theoretical amount) of methylalumoxane were obtained. The molecular weight of this material was measured using the depression of freezing point method in benzene and, at 640, showed an average degree of oligomerization of 11.

(2) Synthesis of Solid Catalyst Component (B)

Silica (1 g, obtained by calcining grade 952 from the Fuji Davison Co. for 4 hours at 300°C) suspended in 10 ml of toluene and 4 ml of a 1 mol/l toluene solution of trimethylaluminium (4 mmol) were added to a 50ml flask which had been thoroughly displaced with nitrogen and reacted for 2 hours at 80°C under a current of nitrogen. Subsequently, 6 ml of a 2.7 mol/l toluene solution of the methylalumoxane (16 mmol) prepared in (1) above were added and reacted for 2 hours. After the

reaction had been completed the solid was isolated using the decantation method and then it was washed thoroughly with toluene, and the solid catalyst component (B-1) was obtained as a toluene slurry. Furthermore, some of this material was taken for analysis and the Al content per 1 g of solid catalyst component was 4.6 mmol.

(3) Propylene Polymerization

Liquid propylene (500 ml) was introduced at room temperature into a 1.5 litre capacity autoclave which had been thoroughly displaced with nitrogen and vacuum dried and then the temperature was raised to 50°C. Then toluene slurry (B-1) which contained the solid catalyst component prepared in (2) corresponding to 0.67 mmol calculated as aluminium atom and ethylenebis(indenyl)zirconium dichloride (2 ml of a 2 mmol/l toluene solution) corresponding to 0.004 mmol calculated as zirconium were introduced and polymerization was carried out for 1 hour. After the polymerization the unreacted propylene was removed, hydrochloric acid/methanol were added and the polymer was filtered off and dried. The recovery of polypropylene obtained in this way was 120 g, the catalyst activity was 30000 g/mmol Zr·hr, and the bulk density of the polymer was 0.37 g/cm³. Moreover, no deposition of polymer inside the autoclave was observed. Furthermore, the mm proportion according the ¹³C-NMR analysis of this polymer was 93.0%. These results are shown in Table 1.

Example 2

Exactly the same procedure as in Example 1 was carried out except that triethylaluminium was used instead of trimethylaluminium in the production of the (B) catalyst component in (2) of Example 1. The results are shown in Table 1

Example 3

Exactly the same procedure as in Example 1 was carried out except that triisobutylaluminium was used instead of trimethylaluminium in the production of the (B) catalyst component in (2) of Example 1. The results are shown in Table 1

Example 4

Exactly the same procedure as in Example 1 was carried out except that methylalumoxane was used instead of trimethylaluminium in the production of the (B) catalyst component in (2) of Example 1. The results are shown in Table 1

Example 5

Exactly the same procedure as in Example 1 was carried out except that isobutylalumoxane was used instead of trimethylaluminium in the production of the (B) catalyst component in (2) of Example 1. The results are shown in Table 1

Example 6

(2) Synthesis of Solid Catalyst Component (B)

A 2.7 mol/l toluene solution (6 ml) of the methylalumoxane (16 mmol) prepared in (1) of Example 1 and 4 ml of a 1 mol/l toluene solution (4 ml) of trimethylaluminium (4 mmol) were added to a 50 ml flask which had been thoroughly displaced with nitrogen and the mixture was heated to 80°C for a period of 2 hours. The whole of this reaction mixture was added to 1 g of silica (obtained by calcining Fuji Davison Co. Grade 952 for 4 hours at 300°C) which had been suspended in 10 ml of toluene and the mixture was reacted for 2 hours at 80°C. After the reaction had been completed the solid was isolated using the decantation method and then it was washed thoroughly with toluene, and the solid catalyst component (B-6) was obtained as a toluene slurry. Furthermore, some of this material was taken for analysis and the Al content per 1 g of solid catalyst component was 4.5 mmol.

(3) Propylene Polymerization

Polymerization was carried out in the same way as in Example 1 except that (B-6) prepared in (2) was used for the solid catalyst component. The results are shown in Table 1

Example 7

Polymerization was carried out in the same way as in Example 1 except that ethylenebis(indenyl)hafnium dichloride was used as the metallocene catalyst component in Example 1. The results are shown in Table 1.

Comparative Example 1

Polymerization was carried out in the same way as in Example 1 except that methylalumoxane corresponding to 0.67 mmol calculated as aluminium was used instead of the solid catalyst component (B-1) in Example 1. The results are shown in Table 1. Moreover, in this case polymer was firmly attached to the inner walls of the autoclave and to the agitator.

Comparative Example 2

Polymerization was carried out in the same way as in Comparative Example 1 except that ethylenebis(indenyl)hafnium dichloride was used as the metallocene catalyst component in Comparative Example 1. The results are shown in Table 1.

Moreover, in this case polymer was firmly attached to the inner walls of the autoclave and to the agitator.

Example 8

Polymerization was carried out in the same way as in Example 1 except that methylenebis(cyclopentadienyl)titanium dichloride was used as the metallocene catalyst component in Example 1. The results are shown in Table 1.

Example 9

Polymerization was carried out in the same way as in Example 1 except that propylenebis(cyclopentadienyl)titanium dichloride was used as the metallocene catalyst component in Example 1. The results are shown in Table 1.

Example 10

Polymerization was carried out in the same way as in Example 1 except that tetramethylenebis(cyclopentadienyl)titanium dichloride was used as the metallocene catalyst component in Example 1. The results are shown in Table 1.

Example 11

Polymerization was carried out in the same way as in Example 1 except that ethylenebis(indenyl)zirconium-1,1'-bi-2-naphtholate was used as the metallocene catalyst component in Example 1. The results are shown in Table 1.

Example 12

Polymerization was carried out in the same way as in Example 1 except that ethylenebis(indenyl)zirconium-4,4'-dimethyl-6,6'-di-1-butyl-2,2'-thiophenolate was used as the metallocene catalyst component in Example 1. The results are shown in Table 1.

Example 13

Polymerization was carried out in the same way as in Example 1 except that tetramethylenebis(indenyl)propoxysirconium chloride was used as the metallocene catalyst component in Example 1. The results are shown in Table 1.

Example 14

Polymerization was carried out in the same way as in Example 1 except that tetramethylenebis(indenyl)butoxysirconium chloride was used as the metallocene catalyst component in Example 1. The results are shown in Table 1.

Table 1

	Solid Catalyst Component	Recovery (g)	Catalyst Activity (g/mmolM•Hr)	Bulk Density (g/cm ³)	mm Proportion (%)
Example 1	B-1	120	30000	0.37	93.0
Example 2	B-2	100	25000	0.37	92.8
Example 3	B-3	80	20000	0.42	94.2
Example 4	B-4	75	18750	0.35	93.5
Example 5	B-5	40	10000	0.38	93.8
Example 6	B-6	80	20000	0.37	92.5
Example 7	B-1	55	13750	0.38	93.2
Example 8	B-1	45	11250	0.37	91.0
Example 9	B-1	35	8750	0.37	91.3
Example 10	B-1	20	5000	0.38	92.6
Example 11	B-1	110	27500	0.36	93.1
Example 12	B-1	100	25000	0.35	93.2
Example 13	-	75	18750	0.36	91.7
Example 14	-	60	15000	0.37	92.6
Comp.Ex.1		100	25000	0.11	92.5
Comp.Ex.2		45	11250	0.08	92.7

Effect of the Invention

When the polymerization of propylene is carried out using the method of this invention the problem of polymer being attached to the reactor does not arise and even when a smaller amount of alumoxane than has been used conventionally is used the activity is high it is possible to obtain highly stereoregular polypropylene which has a good particle properties and a high bulk density.

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